AD-A247 163

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Form Approved
OMB No. 0704-0188

ATE	3. REPORT TYPE AND DATES COVERED
December 1991	Final Report 15 Nov 88 - 14 Nov 91

4. TITLE AND SUBTITLE
New Methodology for Fluorocarbon Synthesis

5. FUNDING NUMBERS
61102F 2303B2

(2)

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AFOSR-TR- 92 0162

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NC
Bolling AFB, DC 20332-6448

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFOSR-89-0134

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Novel, general methods for the preparation of thermally stable perfluorinated organometallic reagents were developed. F-vinyl iodides were prepared as precursors to F-vinyl organometallics. A variety of polyfluorinated cadmium, zinc, and copper reagents were developed as synthetic reagents for the introduction of polyfluorinated alkyl, aryl, and allyl groups. SET chemistry was developed for the regiospecific addition of iodofluoroacetates and iodofluoromethylphosphonates to functionalized alkenes, and to accomplish a useful preparation of allylsulfonyldifluoroacetates and acetamides. Alkylation reactions and acylation reactions of α-fluorocarboxy phoshorus ylides were developed as a useful entry to precursors which could be easily hydrolyzed to α-fluoro ester and α-fluoro-β-keto esters.

14. SUBJECT TERMS

15. NUMBER OF PAGES
40

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIEIED	UNCLASSIFIED	SAR

COMPLETED PROJECT SUMMARY

1. Title: New Methodology for Fluorocarbon Synthesis

2. Principal Investigator: Professor Donald J. Burton
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3. Inclusive Dates: November 15, 1988 - November 14, 1991

4. Grant Number: AFOSR-89-0134

5. Cost and FY Source: $105,655, FY 88
   $108,196, FY 89
   $108,028, FY 90

6. Senior Research Personnel:

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8. Publications:

"Generation of Trifluoromethylcopper from Chlorodifluoroacetate"; J.G. MacNeil, Jr. and D.J. Burton, J. Fluorine Chem., 1992, in press.

"Fluorinated Organometallics: Perfluoroalkyl and Functionalized Perfluoroalkyl Organometallic Reagents in Organic Synthesis"; Z-Y. Yang and D.J. Burton, Tetrahedron Reports, 1992, in press.

"Perfluoroisopropylcadmium and Copper: Preparation, Stability and Reactivity"; H.K. Nair and D.J. Burton, J. Fluorine Chem., 1992, in press.

"A Novel, General Method for the Preparation of α,α-Difluoro Functionalized Phosphonates"; Z-Y. Yang and D.J. Burton, Tetrahedron Lett., 32 (8), 1019 (1991).

"New Approaches to α-Fluoro and α,α-Difluoro Functionalized Esters"; D.J. Burton, A. Thenappan and Z-Y. Yang, ACS Symposium Series #456, "Selective Fluorination in Organic and Bioorganic Chemistry", John Welch, Editor, Chapter 7, 91, 1991.

"A New Approach to α,α-Difluoro-Functionalized Esters"; Z-Y. Yang and D.J. Burton, J. Org. Chem., 56, 5125 (1991).

"Gem-Difluoroallylation of Aldehydes and Ketones as a Convenient Route to α,α-Difluorohomoallylic Alcohols"; Z-Y. Yang and D.J. Burton, J. Org. Chem., 56, 1037 (1991).

"Acylation of Fluorocarbethoxy-Substituted Ylids: A Simple and General Route to α-Fluoro β-Keto Esters"; A. Thenappan and D.J. Burton, J. Org. Chem., 56, 273 (1991).

"Palladium-Catalyzed Reaction of Fluorinated Vinyl Iodides with Terminal Alkynes: A New and General Route to Fluorinated Enynes"; Z-Y. Yang and D.J. Burton, J. Fluorine Chem., 53, 307 (1991).

"Preparation of 1,1,2-Trifluoro-1-Decen-3-Yne"; Z-Y. Yang, P.A. Morken and D.J. Burton, J. Fluorine Chem., 52, 443 (1991).

"The Preparation and Reaction of Fluorinated Phenyl Mono- or Bis-Cadmium and Copper Reagents"; D.J. Burton, Z-Y. Yang and K.J. MacNeil, J. Fluorine Chem., 52, 251 (1991).

"A Facile Method for the Preparation of Allylsulphonyldifluoro-acetates and -acetamides"; Z-Y. Yang and D.J. Burton, J. Chem. Soc. Perkin Trans. 1, 2058 (1991).

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"Sulfonation of [2,3-Dichloropropyl]trifluoroethylene: Synthesis of New Fluorinated β-Sultone and Derivatives"; J. Mohtasham, Z-Y. Yang, D.J. Burton and G.L. Gard, J. Fluorine Chem., 50 (1), 31 (1990).

"Regioselective Preparation of Difluoromethyl Allenes"; D.J. Burton and G.A. Hartgraves, J. Fluorine Chem., 49 (1), 155 (1990).

"Synthesis and Characterization of (E) and (Z)-1,2 Difluoroethenediyl*bis*phosphonates"; L.G. Sprague, D.J. Burton, R.D. Guneratne and W.E. Bennett, J. Fluorine Chem., 49 (1), 75 (1990).

"Preparation of Ethyl 2-Fluoroacrylate, CH_2=CFCOOEt"; A. Thenappan, D.J. Burton, J. Fluorine Chem., 48 153 (1990).

"Reduction-Olefination of Esters: A New and Efficient Synthesis of α-Fluoro-α,β-Unsaturated Esters"; A. Thenappan and D.J. Burton, J.Org. Chem., 55 4639 (1990).

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"Copper Catalyzed Addition Reaction of Iododifluoroacetates To Olefins"; Z-Y. Yang and D.J. Burton, J. Fluorine Chem., 45, 435 (1989).

"A Facile Preparation of Gem-Difluorohomoallylic Alcohols"; Z-Y. Yang and D.J. Burton, J. Fluorine Chem., 44, 339 (1989).

"Preparation of E-1,2,3,3,3-Pentafluoropropene; Z-1,2,3,3,3-Pentafluoropropene, and E-1-Iodopentafluoropropene"; D.J. Burton, T.D. Spawn, P.L. Heinze, A.R. Bailey, and S. Shin-ya, J. Fluorine Chem., 44, 167 (1989).

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"Preparation of α-Fluoro-α,β-unsaturated Esters *Via* Two Carbon Homologation of Esters"; A. Thenappan and D.J. Burton, Tetrahedron Lett., 30 (41), 5571 (1989).

"A Facile Preparation of Ethyl α-Fluoroalkanoates"; A. Thenappan and D.J. Burton, Tetrahedron Lett., 30 (28), 3641 (1989).

"Synthesis of (Sulfodifluoromethyl)phosphonic Acid"; D.J. Burton, A.S. Modak, R.Guneratne, D. Su, W. Cen, R.L. Kirchmeier and J.M. Shreeve, J. Am. Chem. Soc., 111, 1773 (1989).

"Allylations of [(Diethoxyphosphinyl)difluoromethyl]zinc Bromide as a Convenient Route to 1,1-Difluoro-3-alkenephosphonates"; D.J. Burton and L.G. Sprague, J. Org. Chem., 54, 613 (1989).

"The Vibrational Spectrum of Tetrafluoropropyne"; H.B. Friedrich, D.J. Burton and P.A. Schemmer, Spectrochimica Acta, 45A, 181 (1989).

"Fluorine Containing Molecules: Structure, Reactivity, Synthesis and Applications"; J.F. Liebman, A. Greenberg, and W.R. Dolbier, Jr., Eds., VCH Publishers, New York, New York, 1988. Chapter entitled: "Stereospecific Preparation, Reactivity, and Utility of Polyfluorinated Alkenyl Organometallics".

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of this project were: (a) to develop new, novel, stereospecific general methods for the preparation of thermally stable polyfluorinated organometallic reagents. An adjunct of this strategy was to elucidate the structure of these reagents and to develop their application particularly for the synthesis of functionalized fluorocarbon derivatives; (b) to utilize commercially available precursors (where applicable) as the source of fluorine in reactive intermediates in order to facilitate utilization of the synthetic methodology by other workers and to assist scale up of the preparative procedures; (c) to develop single electron transfer (SET) methodology as a useful, easily scaled-up synthesis of functionalized fluorine-containing compounds; (d) to utilize fluorine-containing ylides as synthetic intermediates in the synthesis of α-fluoro-α,β-unsaturated esters; and (e) to develop Pd(0) catalyzed processes for the preparation of perfluoro vinyl or polyfluoroaryl functionalized derivatives.

Initial efforts were directed to the stereospecific preparation of E-vinyl iodides as precursors to E-vinyl organometallics. A successful approach to E-1-iodopentafluoropropene was developed from hexafluoropropene (HFP) *via* reaction of HFP with tertiary phosphines to give the Z-perfluoropropenyl phosphorane. Subsequent hydrolysis of the vinyl phosphorane gave E-1,2,3,3,3-Pentafluoropropene. Treatment of this E-1-hydro-F-propene with SbF_5 gave Z-1,2,3,3,3-Pentafluoropropene. Subsequent metallation of the Z-1-hydro-F-propene (with n-BuLi) and iodination of the organic lithium intermediate gave pure E-1-Iodopentafluoropropene. Trifluorovinyl iodide and both E- and Z-1-iodopentafluoropropenes are stereospecifically converted to the corresponding E-vinyl zinc reagents. These E-vinyl iodides readily participate in Pd(0) catalyzed reactions; with terminal alkynes, we have developed a general stereospecific route to fluorinated enynes. Similarly, fluorinated aryl iodides undergo Pd(0) catalyzed coupling reactions with 1-alkynes and this methodology provides a high yield, easily scaled-up entry to polyfluorinated aryl alkynes and di-ynes.

A variety of polyfluorinated cadmium, zinc and copper reagents have been developed as synthetic reagents for the introduction of polyfluorinated alkyl, allyl and aryl groups. Perfluoroisopropylcadmium and copper were prepared and the stability and reactivity of these secondary perfluoroallyl organometallics was investigated. A new, novel generation of trifluoromethylcopper was developed based on the cheap

precursor, chlorodifluoroacetate. It was also unequivocally demonstrated that trifluoromethylcopper(I) could be cleanly oxidized to a stable trifluoromethylcopper(III) and the first example of a perfluoroalkylcopper(III) complex was prepared and its structure demonstrated by x-ray crystallography. The first preparation of perfluoroallyl cadmium and copper reagents was developed and applications of these novel E-allylic organometallics were demonstrated. Similarly, the facile preparation of E-phenyl Mono- or Bis-cadmium and copper reagents was developed from the commercially available bromo- or iodopentafluorobenzene and 1,2-dibromotetrafluorobenzene, and the application of these novel reagents for the synthesis of functionalized E-aryl derivatives was demonstrated. The first practical preparation of perfluoroalkyl allenes and difluoromethyl allenes was developed from the reaction of perfluoroalkyl copper and difluoromethyl copper reagents with propargyl chlorides and tosylates. In contrast to previous reports, this methodology provided a safe and facile route to these perfluorinated building blocks. The functionalized organometallic, $(RO)_2P(O)CF_2ZnBr$, was developed as a useful stable organometallic reagent and could be utilized in the first, high yield practical synthesis of the novel fluorinated chelating agent, $(RO)_2P(O)CF{=}CFP(O)(OR)_2$ (where R = H, Et). This reagent was also utilized in regiospecific allylation reactions and provided a useful synthetic route to 1,1-difluoro-3-alkenephosphonates. The trifluorovinyl copper reagent was utilized for the development of diene precursors which could be reacted with sulfur trioxide (sulfonation) to give novel fluorinated β-sultones. Ring opening of these sultones gave novel fluorinated sulphonyl fluorides useful in polymerization studies. The commercially available olefin, 3-bromo-3,3-difluoropropene, was utilized in the metal mediated regiospecific gem-difluoroallylation of aldehydes and ketones as an entry to α,α-difluorohomoallylic alcohols. The regiospecificity was correlated with theoretical studies of the 1,1-difluoroallylic anion.

SET chemistry was developed for the regiospecific addition of iododifluoroacetates and iododifluoromethylphosphonates to functionalized alkenes. Reduction of the adducts with a new Ni^0 catalyst provided a practical synthetic route to α,α-difluoro-functionalized esters and α,α-difluoro-functionalized phosphonates. The SET methodology avoided the use of expensive, toxic and hazardous reagents and provided the first practical, easily scaled-up, safe route to these important fluorinated precursors. Similar strategy was utilized to accomplish a useful preparation of allylsulphonyldifluoroacetates and acetamides. A combination of organometallic chemistry and SET chemistry was employed in the preparation of the mixed acid, $(HO)_2P(O)CF_2SO_3H$.

Alkylation and acylation reactions of α-fluorocarboalkoxy phosphorus ylides (phosphonium and phosphonate) were developed as a useful entry to precursors, which could be readily hydrolyzed (aqueous $NaHCO_3$) to α-fluoro ester and α-fluoro-β-keto esters. An adjunct of this strategy resulted in the development of a reduction olefination reaction of fluorinated esters. This methodology provided an efficient synthesis of α-fluoro-α,β-unsaturated esters *directly* from polyfluorinated esters. Thus, the necessity to prepare the easily hydrated and easily polymerized pr ,fluorinated aldehydes was avoided. This methodology was utilized to develop a practical, large scale synthesis of the monomer, ethyl-2-fluoroacrylate.

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution Unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION University of Iowa 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR/NC
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry University of Iowa Iowa City, Iowa 52242	7b. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR 8b. OFFICE SYMBOL (If applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-89-0134
8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.: 61102F PROJECT NO.: TASK NO.: WORK UNIT ACCESSION NO.:

11. TITLE (Include Security Classification)
Generation of Trifluoromethylcopper From Chlorodifluoroacetate

12. PERSONAL AUTHOR(S)
Burton, D.J.; MacNeil, James G.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Preprint/Final	FROM _____ TO _____		5

16. SUPPLEMENTARY NOTATION
J. Fluorine Chemistry, 1992 (in press)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	trifluoromethylcopper; trifluoromethyl aromatics; difluorocarbene

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

In the presence of fluoride ion, methyl chlorodifluoroacetate undergoes halide ion-promoted decarboxylation to give trifluoromethide which can be trapped with cuprous iodide. The resulting trifluoromethyl copper reagent has been observed spectroscopically and can be trapped with aryl iodides to give the corresponding trifluoromethylaromatic compound.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Fred Hedberg	22b. TELEPHONE (Include Area Code) 202-767-496X 22c. OFFICE SYMBOL NC

DD Form 1473, JUN 86 Previous editions are obsolete. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution Unlimited
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6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry University of Iowa Iowa City, Iowa 52242	7b. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR 8b. OFFICE SYMBOL (If applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-89-0134
8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.: 61102F PROJECT NO.: TASK NO: WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Fluorinated Organometallics: Perfluoroalkyl and Functionalized Perfluoroalkyl Organometallic Reagents in Organic Synthesis

12. PERSONAL AUTHOR(S)
Burton, D.J.; Yang, Zhen-Yu

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Preprint/Final	FROM _____ TO _____		88

16. SUPPLEMENTARY NOTATION
Tetrahedron Reports, 1992 (in press)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Fluorinated organometallic reagents

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
A review of the preparation of fluorinated perfluoroalkyl and functionalized perfluoroalkyl organometaliic reagents and their application in organic synthesis.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Fred Hedberg	22b. TELEPHONE (Include Area Code) 202-767-4963
	22c. OFFICE SYMBOL NC

DD Form 1473, JUN 86 Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution Unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION University of Iowa 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR/NC
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8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR 8b. OFFICE SYMBOL (If applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-89-0134
8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.: 61102F PROJECT NO.: TASK NO.: WORK UNIT ACCESSION NO.:

11. TITLE (Include Security Classification)
Perfluoroisopropylcadmium and Copper: Preparation, Stability and Reactivity

12. PERSONAL AUTHOR(S)
Burton, D.J.; Nair, H.K.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Preprint/Final	FROM _____ TO _____		15

16. SUPPLEMENTARY NOTATION
J. Fluorine Chemistry, 1992 (in press)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated organometallics; fluorinated cadmium compounds; fluorinated copper compounds; oxidative addition reactions

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Perfluoroisopropylcadmium can be prepared in excellent yield (98%) from $(CF_3)_2CFI$ and activated cadmium powder in DMF at room tempearture under degassed conditions. The resultant cadmium reagent undergoes metathesis with copper(I)salts to give perfluoroisopropylcopper, in quantitative yield. While perfluoroisopropylcopper is stable in DMF at room temperature under nitrogen, the cadmium counterpart decomposes to a mixture of dimers and trimers of hexafluoropropene, under the same conditions. Sulfur dioxide can be inserted into the cadmium-carbon bond in perfluoroisopropylcadmium while no reaction was observed with the corresponding copper reagent. No stable F-alkylcadmium could be obtained from the reaction of CF_3CF_2CFICF with either Cd powder or Me_2Cd; only the elimination product, $CF_3CF{=}CFCF_3$, was observed. Perfluoroalkylation reactions with F-isopropylcadmium/copper in DMF met with limited success.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Fred Hedberg	22b. TELEPHONE (Include Area Code) 202-767-496X 22c. OFFICE SYMBOL NC

DD Form 1473, JUN 86 Previous editions are obsolete. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

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2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION: University of Iowa; 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: AFOSR/NC
6c. ADDRESS (City, State, and ZIP Code): Department of Chemistry, University of Iowa, Iowa City, Iowa 52242	7b. ADDRESS (City, State, and ZIP Code): Bldg. 410, Bolling AFB, D.C. 20332-6448
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: AFOSR; 8b. OFFICE SYMBOL (If applicable): NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: AFOSR-89-0134
8c. ADDRESS (City, State, and ZIP Code): Bldg. 410, Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. 61102F; PROJECT NO.; TASK NO.; WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
A Novel, General Method for the Preparation of α,α-Difluoro Functionalized Phosphonates

12. PERSONAL AUTHOR(S)
Burton, D.J., Yang, Zhen-Yu

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Final	FROM _____ TO _____		4

16. SUPPLEMENTARY NOTATION
Tetrahedron Letters 32 (8) 1019-1022 (1991)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Phosphonates; fluorinated phosphorus compounds; SET reactions; palladium catalysis

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
The addition reaction of diethyl iododifluoromethylphosphonate to alkenes catalyzed by palladium in the absence of solvent gives the corresponding adducts in good yields at room temperature. A variety of functional groups in the alkenes, including alkyl, trimethylsilyl, hydroxy, epoxy, ketone and ester, are tolerated under the reaction conditions. The reduction of the adducts with nickel chloride and zinc in moist THF provides the title compounds.

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☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL: Dr. Fred Hedberg	22b. TELEPHONE (Include Area Code): 202-767-496X	22c. OFFICE SYMBOL: NC

DD Form 1473, JUN 86 — Previous editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE: Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

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8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR 8b. OFFICE SYMBOL (If applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-89-0134
8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. 61.02F; PROJECT NO.; TASK NO; WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
New Approaches to α-Fluoro and α,α Difluoro Functionalized Esters

12. PERSONAL AUTHOR(S)
Burton, D.J., Thenappan, A., Long, Zhen-Yu

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Final	FROM _____ TO _____		14

16. SUPPLEMENTARY NOTATION
ACS Symposium Series #456, "Selective Fluorination in Organic and Bioorganic Chemistry"; John Welch, Editor, Chapter 7, 91-104 (1991)

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
α-fluoro esters; α,α-difluoroesters; fluorinated esters; SET reactions; fluorinated ylids; alkylation; acylation

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Esters with one or two fluorines at the α-carbon are useful building blocks for construction of interesting and novel biologically active substrates. Alkylation of α-fluorocarboethoxy phosphonium ylides followed by hydrolysis of the resultant phosphonium salt with 5% aqueous sodium bicarbonate provides a useful preparative route to α-fluoroesters. Similarly, acylation/hydrolysis of either α-fluoro phosphonium ylides or α-fluorophosphonate anions gives a general route to 2-fluoro-3-oxo-esters. The α,α-difluoroesters can be prepared by Cu^{0} catalyzed addition of iododifluoroacetates to olefins followed by reduction of the iodo addition adduct. Both terminal and internal olefins participate equally well in the addition reaction.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
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OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution Unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
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8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.: 61102F PROJECT NO.: TASK NO: WORK UNIT ACCESSION NO:

11. TITLE (Include Security Classification)
Gem-Difluoroallylation of Aldehydes and Ketones, as a Convenient Route to α,α-Difluorohomoallylic Alcohols

12. PERSONAL AUTHOR(S)
Burton, D.J.; Yang, Zhen-Yu

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Final	FROM _____ TO _____		5

16. SUPPLEMENTARY NOTATION
J. Organic Chemistry, 56, 1037-1041 (1991)

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Fluoroolefins; fluorinated organometallic reagents; fluorinated homoallylic alcohols; allylation reactions

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

In the presence of zinc, 3-bromo-3,3-difluoropropene or 3-iodo-1,1-difluoropropene reacted with carbonyl compounds to give the corresponding α,α-difluorohomoallylic alcohols in good yields at 0°C to room temperature. The reaction is applicable to aliphatic and aromatic aldehydes, dialkyl ketones, and alkyl aryl ketones. Reaction with α,β-unsaturated aldehydes and ketones yielded 1,2-adducts exclusively. However, the reaction could not be extended to esters and acyl chlorides. Other metals such as cadmium and tin could also be used to mediate gem-difluoroallyliation. The regiochemistry of this reaction could be rationalized in terms of the more nucleophilic α-carbon of the gem-difluoroallyl intermediate.

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11. TITLE (Include Security Classification)
Acylation of Fluorocarbethoxy-Substituted Ylids: A Simple and General Route to α-Fluoro β-Keto Esters

12. PERSONAL AUTHOR(S)
Burton, D.J., Thenappan, A.

13a. TYPE OF REPORT	13b TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Final	FROM _____ TO _____		5

16. SUPPLEMENTARY NOTATION
J. Organic Chemistry, 56, 273-277 (1991)

17. COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Fluorinated Ylids; Fluorinated esters; acylation

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

(Fluorocarbethoxymethylene)tri-n-butylphosphorane (3) reacts with acid chlorides and anhydrides to form the corresponding carbon acylated phosphonium salts 4, and hydrolysis of 4 under mild basic conditions provides RCOCFHCOOEt (8) in moderate yields. The reaction is applicable to primary, secondary, tertiary, cyclic, aromatic, and ester-substituted acid chlorides. Acylation with ethyl chloroformate and ethyl chlorothioformate leads to the diesters $CFH(COOEt)_2$ and EtSCOCFHCOOEt. Extension of this reaction sequence to perfluorinated and partially fluorinated acid chlorides did not proceed cleanly to give the expected phosphonium salts. However, the anion derived from $(EtO)_2P(O)CFHC(O)OEt$ reacts with R_FCOCl to form the corresponding C-acylated phosphonates 10, and hydrolysis of 10 gives $R_FCOCFHCOOEt$.

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11. TITLE (Include Security Classification)
Paladium-catalyzed Reaction of Fluorinated Vinyl Iodides with Terminal Alkynes; A New and General Route to Fluorinated Enynes

12. PERSONAL AUTHOR(S)
Burton, D.J. and Yang, Zhen-Yu

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Final	FROM _____ TO _____		20

16. SUPPLEMENTARY NOTATION
J. Fluorine Chemistry 53, 307-326 (1991)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated eneynes; fluorinated vinyl iodides; fluorine-containing acetylenes; palladium catalysis

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

In the presence of cuprous iodide, the palladium-catalyzed coupling reaction of fluorinated vinyl iodides with terminal alkyl and phenyl substituted alkynes gives the corresponding enynes in good yields under mild conditions. The reaction works well with perfluorovinyl, phenyl and phosphoryl substituted iodides, and the stereochemistry in the vinyl iodide was preserved in the enyne products. With a terminal dialkyne the dienyne is formed when two equivalents of the vinyl iodide are used as substrate. However, upon reaction of Z-iodopentafluoropropene with alkynes containing electron-withdrawing groups such as ethoxycarbonyl or perfluoroalkyl, no desired enynes were observed under similar reaction conditions. The coupling reaction can be carried out in a variety of solvents, including DMF, DMSO, HMPA, acetonitrile, dioxane, chloroform, benzene and hexane as well as in excess triethylamine as solvent.

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11. TITLE (Include Security Classification)
Preparation of 1,1,2-Trifluoro-1-Decen-3-Yne

12. PERSONAL AUTHOR(S)
Burton, D.J.; Yang, Zhen-Yu; Morken, P.A.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Final	FROM _____ TO _____		3

16. SUPPLEMENTARY NOTATION
J. Fluorine Chemistry, 52, 443-445 (1991)

17. COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated eneynes; fluorinated vinyl iodides; fluorine-containing acetylenes

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
The preparation of 1,1,2-Trifluoro-1-Decen-3-Yne via the palladium catalyzed reaction of 1-octyne with trifluorovinyl iodide is described as a general route to fluorinated eneynes.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ OTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
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11. TITLE (Include Security Classification)

The Preparation and Reaction of Fluorinated Phenyl Mono- or Bis-Cadmium and Copper Reagents

12. PERSONAL AUTHOR(S)

Burton, D.J., Yang, Zhen-Yu; MacNeil, Kathryn J.

13a. TYPE OF REPORT	13b TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Final	FROM _____ TO _____		5

16. SUPPLEMENTARY NOTATION

J. Fluorine Chemistry 52, 251-255 (1991)

17. COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated organometallics; aromatic fluorine compounds; fluorinated aryl copper reagents; fluorinated aryl cadmium reagents; fluorinated aryl derivatives

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Tetrafluorodibromobenzenes react readily with acid-washed cadmium in DMF at temperatures ranging from 25° C to 60° C to give bromotetrafluorophenylcadmium reagents in excellent yields. Treatment of the mono- cadmium reagent solution with excess cadmium at 100°C affords the tetrafluorophenylbiscadmium reagents. The mono- and bis-copper reagents are obtained via metathesis of the corresponding cadmium reagents with cuprous bromide at room temperature. Allylation and acylation of the biscopper reagents give the corresponding allylated and acylated tetrafluorobenzenes, respectively.

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11. TITLE (Include Security Classification)
A FAcile Method for the Preparation of Allylsulphonyldifluoro-acetates and Acetamides

12. PERSONAL AUTHOR(S)
Yang, Zhen-Yu and Burton, D.J.

13a. TYPE OF REPORT	13b. TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Final	FROM _____ TO _____		2

16. SUPPLEMENTARY NOTATION
J. Chem. Soc., Perkin Transactions 1, 2058-2059 (1991)

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated ester derivatives; fluorinated amide derivatives; fluorinated sulphones; SET reactions

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
Sulphination of isopropyl bromidifluoroacetate **1a** and N,N-diethyl bromodifluoroacetamide **1b** with sodium dithionite gives compounds **2a** and **2b** respectively which upon cuprous bromide catalysed allylation gave the allylsulphonyldifluoro-acetates and -acetamides.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION Unclassified
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11. TITLE (Include Security Classification): Palladium/cuprous Iodide Catalyzed Coupling of Substituted Tetrafluorophenyl Halides with 1-alkynes

12. PERSONAL AUTHOR(S): Ba V. Nguyen, Z.Y. Yang and D.J. Burton

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		6

16. SUPPLEMENTARY NOTATION: J. Fluorine Chemistry 50, 265-70 (1990)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated organometallics, fluorinated acetylenes, halogenated alkynes, fluorinated aromatics, palladium catalysis

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

In the presence of cuprous iodide, the palladium catalyzed coupling reaction of substituted tetrafluorophenyl halides with 1-alkynes gives the corresponding fluoroaryl alkynes in good to excellent yields under mild conditions. Both 4-substituted (methoxy, N,N-dimethylamino, morpholino) tetrafluorophenyl iodides and bromides work well, and alkyl, trimethylsilyl, phenyl, hydroxy, and ether functionalities in the alkyne moiety are tolerated under the reaction conditions. This methodology provides a practical synthesis of substituted fluorinated aryl alkynes.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ OTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION: unclassified
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11. TITLE (Include Security Classification)
The Preparation and Allylation of Perfluoroallyl Cadmium and Copper Reagents

12. PERSONAL AUTHOR(S)
D.J. Burton, Y. Tarumi and P.L. Heinze

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		7

16. SUPPLEMENTARY NOTATION
J. Fluorine Chemistry, 50, 257-263 (1990)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated organometallics, fluorinated allyl cadmium and copper reagents, perfluoroallyl halides, perfluoro-allylation reactions

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
Perfluoroallyl iodide reacts readily with acid-washed cadmium powder in DMF at 0° C to give the F-allylcadmium reagent. Metathesis of F-allylcadmium with Cu(I)Br at -35° C in DMF gi the F-allylcopper reagent. With zinc powder, perfluoroallyl iodide affords mainly F-1,5-hexadiene. Only a low yield of F-allylzinc was detected. Both F-allylcadmium and F-allylcopper react with allyl bromide to yield 1,1,2,3,3-pentafluoro-1,5-hexadiene.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
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11. TITLE (Include Security Classification)
Sulfonation of [2,3-Dichloropropyl]trifluoroethylene: Synthesis of a New Fluorinated β-Sultone and Derivatives

12. PERSONAL AUTHOR(S)
Mohtasham, J.; Gard, G.L.; Burton, D.J.; Yang, Zhen-Yu

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Final	FROM _____ TO _____		16

16. SUPPLEMENTARY NOTATION
J. Fluorine Chemistry, 50, 31-46 (1990)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluoroolefins; fluorinated sultones; fluorinated acids; fluorinated acid fluorides

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Two new olefins, $CH_2BrCHBrCH_2CF{=}CF_2$ and $CH_2ClCHClCH_2CF{=}CF_2$, have been prepared as precursors to fluoro β-sultones. The new fluorinated sultone, $CH_2ClCHClCH_2CFCF_2OSO_2$, was obtained (from the sulfonation of $CH_2ClCHClCH_2CF{=}CF_2$), along with its rearranged isomer, $CH_2ClCHClCH_2CF(SO_2F)C(O)F$, and hydrolysis product, $CH_2ClCHClCH_2CF(SO_2F)C(O)OH$.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Fred Hedberg	22b. TELEPHONE (Include Area Code) 202-767-496X 22c. OFFICE SYMBOL NC

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SECURITY CLASSIFICATION OF THIS PAGE

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Form Approved OMB No. 07[illegible]88

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2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution Unlimited
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4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
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6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry University of Iowa Iowa City, Iowa 52242	7b. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448
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8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.: 61102F PROJECT NO.: TASK NO.: WORK UNIT ACCESSION NO.:

11. TITLE (Include Security Classification)

Regioselective Preparation of Difluoromethyl Allenes

12. PERSONAL AUTHOR(S)
D.J. Burton and G.A. Hartgraves

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		4

16. SUPPLEMENTARY NOTATION
J. Fluorine Chemistry 49, 155-158 (1990)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated allenes, fluorinated organometallics, fluorinated cadmium reagents

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The difluoromethylcadmium reagent reacts with primary, secondary, and tertiary propargyl chlorides and tosylates regioselectively to give difluoromethyl allenes in good yields.

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22a. NAME OF RESPONSIBLE INDIVIDUAL Frederick L. Hedberg	22b. TELEPHONE (Include Area Code) 202-767-4963 22c. OFFICE SYMBOL NC

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Form Approved OMB No. 0704-0188

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2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; Distribution Unlimited
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11. TITLE (Include Security Classification)
Synthesis and Characterization of (E) and (Z)-1,2-Difluoroethenediyl Bis Phosphonates

12. PERSONAL AUTHOR(S)
L.G. Sprague, D.J. Burton, R.D. Guneratne and W.E. Bennett

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		11

16. SUPPLEMENTARY NOTATION
J. Fluorine Chemistry 49, 75-85 (1990)

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
fluorinated phosphonates, fluorinated organometallics, fluorinated zinc, copper and mercury reagents, fluorinated bisphosphonates and bisphosphonic acids

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
Cuprous halide mediated decomposition of (diethoxyphosphinyl)difluoromethylzinc bromide, $(EtO)_2P(O)CF_2ZnBr$, forms the title bisphosphonates in 50% isolated yield. The ^{19}F and ^{31}P NMR spectra of these isomeric bisphosphonates exhibit non-first order AA'XX' patterns. Computer simulation permitted the determination of the J_{P-F}, J_{F-F}, and J_{P-P} coupling constants for these compounds. Silylation and hydrolysis of the bisphosphonate mixture gave the silylated bisphosphonates and bisphosphonic acids respectively, as expected. Metathesis of the zinc reagent also yielded phenyl (diethoxyphosphinyl)difluoromethylmercury, $(EtO)_2P(O)CF_2HgPh$, in good yield. However, attempts to generate fluoro(diethoxyphosphinyl)carbene from this mercurial were unsuccessful.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☑ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified

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8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.: 61102F PROJECT NO.: TASK NO.: WORK UNIT ACCESSION NO.:

11. TITLE (Include Security Classification)
Preparation of Ethyl 2-Fluoroacrylate, $H_2C{=}CFCO_2Et$

12. PERSONAL AUTHOR(S)
A. Thenappan and D.J. Burton

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
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16. SUPPLEMENTARY NOTATION
J. Fluorine Chemistry 48, 153-157 (1990)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated esters, fluorinated monomers, unsaturated fluorinated ester, fluorinated carbanions, fluorinated phosphonate anions

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

From ethyl formate, a large scale preparation of ethyl 2-fluoroacrylate has been developed. This work provides the most straightforward, one-step, highest yield synthesis of this monomer.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
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8c. ADDRESS (City, State, and ZIP Code): Bldg. 410, Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. 61102F; PROJECT NO.; TASK NO.; WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Reduction-olefunction of Esters: A New and Efficient Synthesis of α-Fluoro-α,β-Unsaturated Esters

12. PERSONAL AUTHOR(S)
A. Thenappan and D.J. Burton

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		4

16. SUPPLEMENTARY NOTATION
J. Organic Chemistry 55, 4639-4642 (1990)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated esters, fluorinated phosphonate ylids, fluorinated carbanions, unsaturated fluorinated esters, fluorinated aldehydes

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A reduction-olefination sequence has been used to convert esters to α-fluoro α,β-unsaturated esters. In the presence of diisobutylaluminum hydride, esters are reduced to aldehydes that react in situ with $[(EtO)_2P(O)CFC(O)OEt]^-Li^+$ to form the title compounds in good yields with high stereoselectivity. The reaction is applicable to aliphatic, aromatic, cyclic, unsaturated, perfluorinated, and partially fluorinated esters. The E/Z ratio of unsaturated esters formed in the reaction varies with the cations present in the reaction mixture. Solvents have very little influence on stereochemistry. The sequential transformation of $PhC(O)OBu^n$ to (E)-PhCH=CFC(O)OEt and then to (E,E)-PhCH=CFCH=CFC(O)OEt illustrates the scope of this methodology, which introduces a fluorine atom adjacent to an ester functionality with concomitant elongation of the chain by two carbon atoms.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified
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11. TITLE (Include Security Classification)
A Facile, General Route to Perfluoroalkyl Allenes

12. PERSONAL AUTHOR(S)
D.J. Burton, G.A. Hartgraves and J. Hsu

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		4

16. SUPPLEMENTARY NOTATION
Tetrahedron Letters 31 (26) 3699-3702 (1990)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Fluorinated copper reagents, fluorinated organometallics, fluorinated allenes

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Perfluoroalkyl copper reagents react with propargyl halides or tosylates in DMF or DMSO at 0°C-RT to afford perfluoroalkyl allenes regiospecifically in good yield.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified
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11. TITLE (Include Security Classification)
A Facile, General Method for the Preparation of Fluorinated Enynes

12. PERSONAL AUTHOR(S)
Burton, D.J.; Yang, Zhen-Yu

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		4

16. SUPPLEMENTARY NOTATION
Tetrahedron Letters 31 (10) 1369-1372 (1990)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Fluorinated acetylenes; fluorinated olefins; palladium catalysis; fluorinated vinyl halides; coupling reactions

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
Fluorinated vinyl iodides, $R^1CF{=}CFI$ [where $R^1{=}F$, CF_3, Ph, $(^iPrO)_2P(O)$], couple directly with 1-alkynes in the presence of palladium and cuprous iodide in triethylamine to give excellent yields of the fluorinated enynes.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Fred Hedberg	22b. TELEPHONE (Include Area Code) 202-767-496X 22c. OFFICE SYMBOL NC

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11. TITLE (Include Security Classification)
Alkylation of (Fluorocarbethoxymethylene)tri-n-butylphosphorane: A Facile Entry to α-Fluoroalkanoates

12. PERSONAL AUTHOR(S)
Burton, D.J.; Thenappan, A.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim.	FROM _____ TO _____		7

16. SUPPLEMENTARY NOTATION
J. Organic Chemistry 55 (8), 2311-2317 (1990)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	α-fluoroesters; fluorinated ylides; alkylation; α-fluorophosphoranes

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

(Fluorocarbethoxymethyl)trialkylphosphonium bromides, prepared from ethyl bromofluoroacetate and tertiary phosphines, react with n-butyllithium in THF to give the corresponding phosphoranes. Reaction of the pregenerated (fluorocarbethoxymethylene)tri-n-burylphosphorane with primary alkyl iodides and activated alkyl bromides followed by in situ hydrolysis of the alkylated salts provides the fluoroalkanoates in a one-pot reaction. In the case of secondary alkyl halides, no substitution was observed, the main reaction being decomposition of the phosphorane. However, the anion obtained from diisopropyl (fluorocarbethoxymethyl)phosphonate reacts with $CH_3CH(Ph)Br$ and $(CH_3)_2CHI$ to afford the corresponding alkylated phosphonates in good yields. Displacement of the phosphonate moiety either by base-induced hydrolysis or by reduction was unsuccessful.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
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SECURITY CLASSIFICATION OF THIS PAGE

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11. TITLE (Include Security Classification)
Synthesis and X-ray Structure of Bis(Trifluoromethyl)(N,N-diethyldithiocarbamato)copper; A Remarkably Stable Perfluoroalkylcopper(III) Complex

12. PERSONAL AUTHOR(S)
Burton, D.J.; Willert-Porada, M.A.; Baenziger, N.C.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		2

16. SUPPLEMENTARY NOTATION
J,. Chemical Society, Chemical Communications 1633-1634 (1989)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Perfluoroalkyl copper, Copper (III) Complexes; Trifluoromethyl organometallics

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
The reaction between trifluoromethylcadmium reagent and $Br_2Cu(edtc)$ (edtc = N,N-diethyldithiocarbamato) or $CdI^+[(CF_3)_2Cu]^-$ with $[Et_2NC(S)S]_2$ in DMF (dimethylformamide) at -30°C yields the stable Cu^{III} perfluoroalkylcopper complex, $(CF_3)_2CuSC(S)NEt_2$.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Fred. Hedberg	22b. TELEPHONE (Include Area Code) 202-767-496X 22c. OFFICE SYMBOL NC

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11. TITLE (Include Security Classification)

Copper Catalyzed Addition Reaction of Iododifluoroacetates to Olefins

12. PERSONAL AUTHOR(S)
Burton, D.J.; Yang, Zhen-Yu

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		5

16. SUPPLEMENTARY NOTATION
Journal of Fluorine Chemistry 45, 435-439 (1989)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated esters; organometallic reagents single electron transfer reactions

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The addition of iododifluoroacetates to alkenes is catalyzed by copper powder (10-20 mol %) at 50° to 60°C. The reaction can be carried out neat or in hexane or benzene as solvent. Both terminal and internal alkenes gave good yields (65-83%). Reduction of the adduct with tributyltin hydride provides the α,α-difluoroacetate.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ OTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Fred Hedberg	22b. TELEPHONE (Include Area Code) 202-767-496X 22c. OFFICE SYMBOL NC

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Form Approved OMB No. 0704-0188

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2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release
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6a. NAME OF PERFORMING ORGANIZATION University of Iowa 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR/NC
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8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR 8b. OFFICE SYMBOL (If applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-89-0134
8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.: 61102F PROJECT NO.: TASK NO.: WORK UNIT ACCESSION NO.:

11. TITLE (Include Security Classification)
A Facile Preparation of Gem-Difluorohomoallylic Alcohols

12. PERSONAL AUTHOR(S)
Zhen-Yu Yang and Donald J. Burton

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		

16. SUPPLEMENTARY NOTATION
Journal of Fluorine Chemistry, 44 339-343 (1989)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated alcohols, fluorine-containing olefins, organometallics, homoallylic alcohols, allylation reactions

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The reaction of 3-bromo-3,3-difluoropropene with zinc powder in THF at 0°C to room temperature in the presence of aldehydes and ketones provides a useful, easily scaled up route to gem-difluorohomoallylic alcohols. α,β-Unsaturated aldehydes and ketones give exclusively the 1,2-addition product. In all cases, only the α-gem-difluorohomoallyl regioisomer was observed.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
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22a. NAME OF RESPONSIBLE INDIVIDUAL Anthony J. Matuszko	22b. TELEPHONE (Include Area Code) 202-767-496X 22c. OFFICE SYMBOL NC

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8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.: 61102F PROJECT NO.: TASK NO.: WORK UNIT ACCESSION NO.:

11. TITLE (Include Security Classification)
Preparation of E-1,2,3,3,3-Pentafluoropropene, Z-1,2,3,3,3-Pentafluoropropene and E-1-Iodopentafluoropropene

12. PERSONAL AUTHOR(S)
D.J. Burton, T.D. Spawn, P.L. Heinze, A.R. Bailey and S. Shin-Ya

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
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16. SUPPLEMENTARY NOTATION
Journal of Fluorine Chemistry, "Fluorine Chemistry Synthesis", 44 167-174 (1989)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Fluoroolefins, iodofluoroolefins, fluoro phosphoranes, fluoro organometallics

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

From hexafluoropropene, large scale stereospecific syntheses have been developed for the preparation of E-$CF_3CF{=}CFH$, Z-$CF_3CF{=}CFH$ and E-$CF_3CF{=}CFI$.

This work provides the 1st stereospecific preparation of 1-hydro and 1-iodo alkenes.

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11. TITLE (Include Security Classification)
Am Expedient Synthesis of α-Fluoro-β-Ketoesters

12. PERSONAL AUTHOR(S)
Burton, D.J.; Thenappan, A.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
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16. SUPPLEMENTARY NOTATION
Tetrahedron Letters 30 (45) 6113-6116 (1989)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated ylides; α-fluoroesters; fluorinated β-ketoesters; acylation, fluorinated phosphoranes

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
Acylation of fluorocarboethoxymethylene tri-n-butylphosphorane followed by hydrolysis under mild basic conditions provides the title compounds in good yields.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
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22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Fred Hedberg	22b. TELEPHONE (Include Area Code) 202-767-496X 22c. OFFICE SYMBOL NC

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8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. 61102F; PROJECT NO.; TASK NO.; WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
Preparation of α-Fluoro-α,β-Unsaturated Esters via Two Carbon Homologation of Esters

12. PERSONAL AUTHOR(S)
Alagappan Thenappan and Donald J. Burton

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		

16. SUPPLEMENTARY NOTATION
Tetrahedron Letters, 30 (41) 5571-5574 (1989)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluoro esters, unsaturated fluoro esters, fluorinated aldehydes, phosphoranes, ylides

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
In the presence of diisobutyl aluminum hydride, esters react with an anion derived from $(EtO)_2P(O)CFHC(O)OEt$ to give the title compounds in good yields. The scope of this method and the factors which influence the stereochemistry of the products are discussed.

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22a. NAME OF RESPONSIBLE INDIVIDUAL Anthony J. Matuszko	22b. TELEPHONE (Include Area Code) 202-767-496X 22c. OFFICE SYMBOL NC

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8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR 8b. OFFICE SYMBOL (If applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFPSR-89-0134
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11. TITLE (Include Security Classification)
Preparation of α-Fluoro-α,β-Unsaturated Esters via Two Carbon Homologation of Esters

12. PERSONAL AUTHOR(S)
Alagappan Thenappan and Donald J. Burton

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
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16. SUPPLEMENTARY NOTATION
Tetrahedron Letters, 30 (41) 5571-5574 (1989)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluoro esters, unsaturated fluoro esters, fluorinated aldehydes, phosphoranes, ylides

19. ABSTRACT (Continue on reverse if necessary and identify by block number)
In the presence of diisobutyl aluminum hydride, esters react with an anion derived from $(EtO)_2P(O)CFHC(O)OEt$ to give the title compounds in good yields. The scope of this method and the factors which influence the stereochemistry of the products are discussed.

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8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. 61102F; PROJECT NO.; TASK NO.; WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
A Facile Preparation of Ethyl-α-Fluoroalkanoates

12. PERSONAL AUTHOR(S)
Alagappan Thenappan and Donald J. Burton

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		

16. SUPPLEMENTARY NOTATION
Tetrahedron Letters, 30 (28) 3641-3644 (1989)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluoro esters, ylides, alkylations, phosphoranes, fluorophosphoranes

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Alkylation of fluorocarboalkoxymethylene tri-n-butylphosphorane followed by hydrolysis provides the title compounds in moderate to good yields.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ OTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
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11. TITLE (Include Security Classification)
Synthesis of (Sulfodifluoromethyl)Phosphonic Acid

12. PERSONAL AUTHOR(S)
Burton, D.J., Modak, A.S., Guneratne, R., Su, D., Cen, W., Kirchmeier, R.L., Shreeve, J.M.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		4

16. SUPPLEMENTARY NOTATION
J. Am. Chem. Soc., 111, 1773-1776 (1989)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Fluorinated phosphonic acid; fluorinated sulfonic acid; super acids

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

(Sulfodifluoromethyl)phosphonic acid, $(HO)_2P(O)CF_2SO_3H$, has been synthesized for the first time. This mixed phosphonic-sulfonic acid was prepared from $(C_2H_5O)_2P(O)CF_2SO_3Na$, which had been synthesized via oxidation of the corresponding sulfinate salt, $(C_2H_5O)_2P(O)CF_2SO_2Na$. The sulfinate salt was prepared from $(C_2H_5O)_2P(O)CF_2X$(X = Br,I) and $[(C_2H_5O)_2P(O)CF_2SO_2]_2Cd$ precursors.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ OTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
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11. TITLE (Include Security Classification)
Alkylations of [(Diethoxyphosphenyl)difluoromethyl]zinc Bromide as a Convenient Route to 1,1-Difluoro-3-alkenephosphonates

12. PERSONAL AUTHOR(S)
Burton, Donald J., Sprague, Lee G.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
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16. SUPPLEMENTARY NOTATION
J. Organic Chemistry, 54, 613-617 (1989)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	fluorinated organometallics; fluorinated phosphonates; fluorinated zinc reagents.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The reaction of [(diethoxyphosphinyl)difluoromethyl]zinc bromide, $(EtO)_2P(O)CF_2ZnBr$, with allylic halides was found to be catalyzed by CuBr and represents a synthetically viable and convenient route to the title phosphonates. However, the reaction could not be readily extended to allyl acetate. Propargyl chloride gave predominantly an allenic product, diethyl 1,1-difluoro-2,3-butadienephosphonate (4). The regiochemistry of the allylation reactions is controlled by steric factors such that the $(EtO)_2P(O)CF_2$ moiety is bound to the least sterically hindered allylic terminus. Evidence is presented for an S_N2 vs S_N2' type mechanistic interpretation, rather than the involvement of a symmetrical (π-allyl)Cu(III) intermediate and an oxidative addition/reduction elimination type mechanism.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
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8c. ADDRESS (City, State, and ZIP Code): Bldg. 410 Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. 61102F; PROJECT NO.; TASK NO.; WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
The Vibrational Spectrum of Tetrafluoropropyne

12. PERSONAL AUTHOR(S)
Friedrich, H.Bruce, Burton, Donald J., Schemmer, Pamela A.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Reprint/Interim	FROM _____ TO _____		5

16. SUPPLEMENTARY NOTATION
Spectrochimica Acta, 45A (2) 181-185 (1989)

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Fluorinated acetylenes, acetylenes, IR spectrum

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The i.r. spectrum of gaseous tetrafluoropropyne has been measured from 4000 to 100 cm^{-1}, and all of the observed bands have been assigned. The C mode frequencies of the CF_3 group are similar to those of other CF_3CCX species, and even though the a_1 modes are less regular, the variations can be explained without changes in force constants other than those involving the C-X bond. Several bands, particularly ν_1 and combinations with ν_1, show pronounced sequence structure due to excited levels of ν_{10}, the C-C-C skeletal bend.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ OTIC USERS	Unclassified
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4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION University of Iowa 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION AFOSR/NC
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry University of Iowa Iowa City, Iowa 52242	7b. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448
8a. NAME OF FUNDING, SPONSORING ORGANIZATION AFOSR 8b. OFFICE SYMBOL (If applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-89-0134
8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling AFB, D.C. 20332-6448	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO.: 61102F PROJECT NO.: TASK NO.: WORK UNIT ACCESSION NO.:
11. TITLE (Include Security Classification) Stereospecific Preparation, Reactivity and Utility of Polyfluorinated Alkenyl Organometallics	
12. PERSONAL AUTHOR(S) Burton, Donald J.	
13a. TYPE OF REPORT Book Chapter/Interim 13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) 15. PAGE COUNT 16
16. SUPPLEMENTARY NOTATION "Fluorine-Containing Molecules", Structure, Reactivity, Synthesis and Applications; Eds., Liebman, Greenberg and Dolbier, VCH Publishers, 1988; Chapter 8.	
17. COSATI CODES FIELD / GROUP / SUB-GROUP	18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) fluorinated organometallics, fluorinated vinyl organometallics, fluorinated alkenyl zinc, cadmium and copper reagents

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A review chapter concerning the synthesis, chemical reactivity and synthetic applications of fluorinated vinyl zinc, cadmium and copper reagents, with particular emphasis on stereospecificity and stereochemical control.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Anthony J. Matuszko	22b. TELEPHONE (Include Area Code) 202-767-496X 22c. OFFICE SYMBOL NC

DD Form 1473, JUN 86 — Previous editions are obsolete. — SECURITY CLASSIFICATION OF THIS PAGE: Unclassified